Photoelectrochemical Properties and Microstructuring of Polythiophenes

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Photoelectrochemical microstructuring processes have been known for various classes of semiconductors including intrinsically conducting polymers [1]. In this work, a new technique was developed of directional photoelectrochemical post-structuring of conducting polymers deposited on Pt and p-Si. The technique utilizes the ability of polythiophene polymers to undergo photoelectrochemically induced cathodic doping in a non-aqueous solution in the presence of tetrabuthylammonium (TBA) salts [2,3]. Figure 1 presents cyclic voltamogram of one of the investigated polymers, poly-3-phenylthiophene, in a TBA –based solution. Characteristic cathodic peaks suggest that the polymer can be cathodically doped in these conditions. This is also demonstrated by the evolution of the UV-vis adsorption spectra taken in-situ in the course of cathodic doping (Fig.2). Under illumination, the film can be also cathodically doped but at potentials insufficient for the ordinary cathodic doping. The occurrence of the photoelectrochemical cathodic doping was in particular demonstrated by in-situ conductivity measurements.

In this work, local photoelectrochemical cathodic doping was performed by illuminating the polymer surface with a focused laser beam. This allowed creation of patterns of locally conducting polymer surrounded by an insulating (semiconducting) polymer phase. Poly-3-phenylthiophene (P3PhT) and polybithiophene (PBT) as well as some derivatives of poly-3,4-ethylenedioxythiophene (PEDOT) were investigated. In the case of P3PhT and the PEDOT derivative, colorless conducting films are formed, and the post-structuring process could be visualized using conventional optical microscopy. However, in principle, this technique can be applied to the other polymers of the thiophene series as well, for which the occurrence of the photostimulated cathodic doping was demonstrated [2,3].

An example of obtained micropatterns is shown in Fig. 3. The resolution of the micropatterning was as low as 5 μm. Both for metal and semiconducting supports, the micropatterning could be performed in potentiostatic and in open-circuit conditions, without applying external bias. The obtained micropatterns were stable in air and in the anodic doping region, but could be removed by repeated cycling encompassing the regions of both anodic and cathodic doping. The microstructures were characterized by SEM, EDAX, SECM and other techniques.

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REFERENCES

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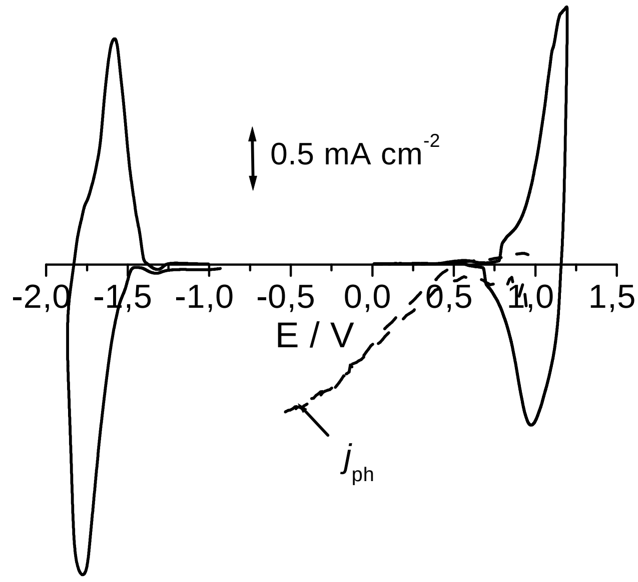

Fig.1. Cyclic voltamograms for a 120-nm P3PhT film taken in 0.1 M Bu_4NBF_4 in acetonitrile. The scan rate was 50 mVs^{-1}, the potential values are presented vs. SCE (aq.). Also shown in the figure is the photocurrent-potential dependence (dashed line, illumination with a 488-nm chopped light, *f* = 220 Hz). The photocurrent has cathodic direction and is presented in arbitrary units.

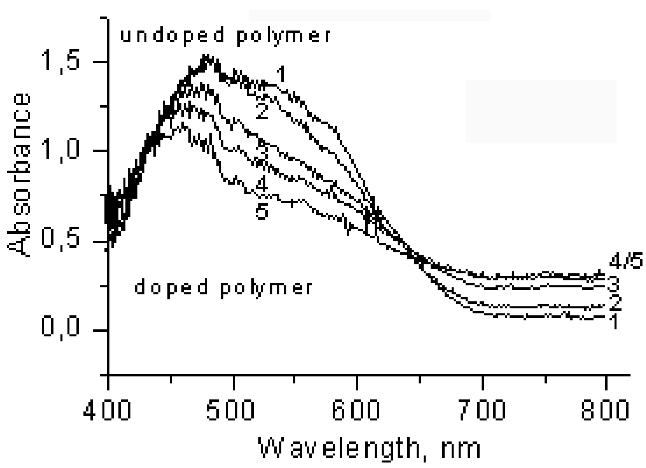

Fig.2. In-situ UV-vis absorption spectra for a 120-nm P3PhT film on ITO glass substrate taken in the course of the cathodic doping at a potential of (1) –0.5 V, (2) –1.5 V, (3) -1.6 V, (4) -1.65 V, (5) –1.75 V.

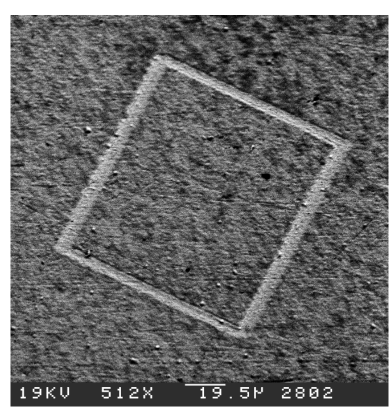

Fig. 3. SEM image of a 100 μm × 100 μm rectangular pattern obtained by repeatedly scanning the focused laser beam (Ar^+ laser, Spectra Physics, λ = 488 nm, P = 2.5 mW) over the surface of a 120-nm P3PhT film on Pt in TBA-based propylene carbonate solution. The film was held at a potential of –0.5 V (aq. SCE).